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ACADEMICIAN ALEKSANDR YERMININGEL'DOVICH ARBUZOV

B. A. Kazanskiy and M. I. Kabachnik

Aleksandr Yerminingel'dovich Arbuzov, one of the outstanding Soviet organic chemists was born 12 September (30 August, old-style calendar) 1877 in the village of Arbuzovo-Baran, in Spasskiy Uyezd, Kazanskaya Guberniya. He received his primary education in the village school, and then in the first Kazan' Classical Gymnasium, which he left in 1896, whereupon he immediately entered the Natural Science Division of the Physics and Mathematics Faculty of Kazan' University. Here, as a student, he completed his first scientific work under the guidance of Professor A. M. Zaytsev, "On Allyl-Methyl-Phenyl-Carbinol," which was published in the Journal of the Russian Physics and Chemistry Society in 1901.

Upon completion of university studies in 1900, Arbuzov was recommended by Professor A. M. Zaytsev for a teaching fellowship with Kazan' University. However, he did not wait for confirmation of the appointment, and accepted a position as assistant in the Institute of Agriculture and Forestry in Novaya Aleksandriya.

In 1905, Arbuzov passed his master's examinations and defended his master's dissertation on the subject, "The Structure of Phosphorous Acid and Its Derivatives," for which the Russian Physics and Chemistry Society awarded him the Zinin and Voskresenskiy Prize, and which helped him to earn recognition among Russian chemists.

In 1906, Arbuzov was appointed assistant professor at the Novoaleksandriyskiy Institute, and in 1911, after the death of his teacher, A. M. Zaytsev, he was appointed extraordinary professor (professor adjunct) of Kazan' University, where he occupied the chair of his famous predecessors, N. N. Zinin, A. M. Butlerov, and A. M. Zaytsev. After defending his doctor's dissertation, "On the Phenomena of Catalysis in Transformations of Certain Phosphorus Compounds," he received a permanent appointment as

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full professor, and all his subsequent scientific and pedagogic activity, up to now, has been connected with Kazan' University and other higher educational institutions in Kazan'.

From 1921 to 1923, he was dean of the Physics and Mathematics Faculty; from 1923 to 1925, a member of the Educational Board; and since 1929, a permanent director of the Scientific Research Institute of Chemistry imeni A. M. Butlerov at Kazan' University. Since 1930, Arbuzov has occupied the chair for Organic Chemistry at Kazan' Institute of Chemical Technology, in the organization of which he took active part. In 1932, he was elected Corresponding Member, and in 1942, Active Member of the Academy of Sciences USSR. For his outstanding scientific work, Arbuzov has twice won the Stalin prize, and for his scientific and pedagogic activity, he has twice received the Order of Lenin.

With the organization in 1945 of an Affiliate of the Academy of Sciences USSR in Kazan', Arbuzov was elected its President; in 1946, the workers of the Zelenodol'skiy electoral district elected him as their Deputy in the Council of Nationalities of the Supreme Soviet USSR.

Among Arbuzov's numerous works, which are varied in subject and deal not only with different sections of organic chemistry but also with problems of physical chemistry and the history of chemistry, the most important work is his research on organic phosphorus compounds. His investigations are remarkable for their orderly system, integrity and consistency, and it is possible to divide them into several groups only in a limited sense.

The first group, chronologically speaking, includes research work connected with the synthesis and study of the properties of esters of acids formed by trivalent phosphorus, primarily phosphorous acid, which was carried out in its basic stages before the October Revolution. The preparations of phosphorous acid esters repeatedly described by other authors before Arbuzov's works were all complex mixtures containing only a small proportion of esters of the $P(OR)_3$ class.

Arbuzov was the first to synthesize in a pure form full alkyl esters of phosphorous and phenyl-phosphinic acids, demonstrating in his early work the high degree of skill which became so characteristic of all his later experimental research.

The method of synthesis, originally worked out by Arbuzov and consisting of the reaction of solid alcoholates not containing spirits with phosphorous trichloride according to the equation

$$3RONa + PCl_3 \rightarrow (RO)_3\ P + NaCl$$

is now merely of historical interest. However, even the contemporary, generally accepted method of obtaining the esters of phosphorous acid may be ascribed to Arbuzov. Shortly before World War II, it was elaborated upon by his student, K. V. Nikanorov, and is a modification of Milobendzkiy and Sakhnovskiy's method, consisting of the reaction of alcohols with phosphorous trichloride in the presence of dimethyl aniline:

$$3ROH + PCl_3 + 3C_6H_5N(CH_3)_2 \rightarrow (RO)_3\ P + 3C_6H_5N(CH_3)_2 \cdot HCl$$

The most important result of research done by Arbuzov on the esters of phosphorous acid was the discovery of their capacity to rearrange themselves, under the influence of alkyl halides, into esters of phosphinic acids with the formation of the C-P link. This reaction, which is called the Arbuzov regrouping is expressed in the following scheme established by him:

$$R'J + P(OR)_3 \rightarrow \begin{matrix} R' \\ J \end{matrix} > P(OR)_3$$

$$\begin{matrix} R' \\ J \end{matrix} > P(OR)_3 \longrightarrow RJ + R'-P(OR)_2=O$$

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In the reaction with an alkyl halide, containing a radical analogous to the radical of a phosphorous ester (R = R'), the regrouping becomes isomerization. It can be caused by a very small amount of alkyl halide, which regenerates in the process of reaction and acts as a catalyzer. Arbuzov's reaction became one of the most important methods of synthesis of the organic compounds of phosphorus; with the aid of this method he was able to synthesize esters of primary and secondary alkyl-phosphinic and alkylarylphosphinic acids and the acids themselves, phosphocarboxylic acid, phosphoacetophenone, compound oxides of tertiary phosphines, and many other organic compounds of phosphorus.

In particular, Arbuzov together with his students (A. A. Dunin, A. I. Razumov), carried out the synthesis of phosphoacetic ester--the phosphorus analogue of acetoacetic ester, which has the property similar to the latter, of producing metallic derivatives under the action of potassium or sodium; with these metallic derivatives it is possible to carry out syntheses, analogous to the syntheses with acetoacetic ester.

The reaction of regrouping made it possible for Arbuzov, to obtain organic compounds of phosphorus containing an asymmetric atom of phosphorus in the molecule. This work was carried out in collaboration with B. A. Arbuzov, I. A. Arbuzova, and G. Kh. Kamay.

In close connection with the study of the properties of phosphorous acid esters is the work of Arbuzov in relation to the tautomerism of dialkyl esters of phosphorous acid and the reactions of their metallic derivatives. These esters may have the structure $P(OR)_2(OH)$ or $HPO(OR)_2$, i.e., they may be derivatives both of the triple-hydroxyl or double-hydroxyl form of phosphorous acid. Michaelis and Becker's well-known reaction of a sodium derivative of dialkyl phosphorous acid with the alkyl halides, which results in the formation of esters of alkyl-phosphinic acids with a pentavalent atom of phosphorus

$$(RO)_2\,PONa + R'I \rightarrow NaI + R'\text{-}P(=O)(OR)(OR)$$

cannot serve as proof of the fact that the initial dialkyl phosphorous ester contains phosphorus in a pentavalent state, as it is possible to conceive the formation $R'\text{-}P(=O)(OR)(OR)$ also from a form with a trivalent atom of phosphorus.

In developing his former work, Arbuzov studied the course of this reaction in detail in relation to the nature of the metal and the type of the halogen derivative. It appeared that the reaction most frequently takes place with the formation of phosphinic acid derivatives; as for example, triphenylchloromethane with sodium diethylphosphite reacts according to the equation:

$$(C_6H_5)_3CCl + NaOP(OC_2H_5)_2 \rightarrow (C_6H_5)_3C\text{-}P(=O)(OC_2H_5)_2 + NaCl$$

The formation of full compound ester of phosphorous acid is also possible, and can be observed in the reaction of silver diethylphosphite with Triarylmethyl chloride:

$$(C_2H_5O)_2\,POAg + ClCAr_3 \rightarrow (C_2H_5O)_2P(OCAr_3) + AgCl$$

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Finally, in the reaction of triarylmethyl bromides with alkaline salts of diethyl phosphorous acid instances of an anomalous course of this reaction with the formation of free triarylmethyl radicals were discovered:

$$(C_2H_5O)_2\,PONa + BrCAr_3 \rightarrow NaBr + (C_2H_5O)_2\,PO + CAr_3.$$

The consideration of different experimental results enabled Arbuzov to develop the idea of tautomerism of dialkyl phosphorous acids and to draw a far-reaching parallel with tautomerism of ketoenols, lactimlactams, etc. All of this research carried out by him and his students was summarized by him in a brilliant report, which was read at the December session of the Academy of Sciences in 1936, "The Problem of the Mechanism of Reactions of the Double Exchange of Metallic Derivatives of Tautomeric Organic Compounds."

One of the conclusions made by Arbuzov at the end of his report was to acknowledge the necessity of further experimental and theoretical study of tautomerism, making use of the latest physical and chemical methods of studying the structure of matter. Quite recently (in collaboration with M. I. Batuyev and V. S. Vinogradova), he published a work, wherein the problem of tautomerism of dialkyl phosphorous acid is solved by means of the spectral method.

The study of spectra of combination light dispersion has shown that liquid dialkyl phosphorous acids contain predominantly an element with a P-H link, corresponding to the double-hydroxyl form of phosphorous acid. However, the spectrum likewise reveals the presence of O-H combinations, which corresponds to the triple-hydroxyl form of phosphorous acid. At the same time the cyclic association of molecules of dialkyl phosphorous acid was established.

An interesting section of A. Ye Arbuzov's work is his study (in collaboration with B. A. Arbuzov) of the so-called Boyd chloranhydride. It would have been possible to ascribe two structural formulas to this substance, which has very unusual properties:

$$(C_6H_5)_3C\text{-}O\text{-}PCl_2 \quad \text{and} \quad (C_6H_5)_3\,C\text{-}\underset{\underset{O}{\|}}{P}Cl_2$$

A. Ye. and B. A. Arbuzov have worked out an excellent method of obtaining this chloranhydride, and have studied its various transformations in detail, presenting weighty arguments in favor of the second formula, which was later definitely confirmed by Katt, a student of Boyd. In A. Ye. Arbuzov's laboratory, many analogues of Boyd's chloranhydride have been prepared (K. V. Nikanorov).

In studying Boyd's chloranhydride, A. Ye. and B. A. Arbuzov discovered a new method of obtaining free radicals, which was mentioned above With the aid of this method, it was possible to synthesize several free radicals, not previously described. The new method is so superior in its ease of practicable application that A. Ye. Arbuzov recommends it for demonstration purposes during lectures.

Finally, we might mention a group of experiments by A. Ye. Arbuzov in connection with the preparation of esters of subphosphoric, pyrophosphoric and pyrophosphorous acids. This work followed the study of reactions in the formation of free radicals, but it has its own independent value. The

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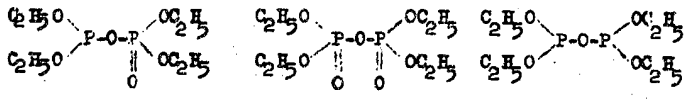
above-mentioned esters were obtained by the reaction of sodium diethyl phosphite with bromine.

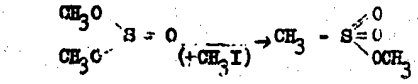
A careful study of the reaction products enabled A. Ye. and B. A. Arbuzov to isolate individual esters from the very complex structure, and with the aid of a series of reactions to establish the following structural formulas:



It is impossible in this outline to mention even in passing, all Arbuzov's work on the organic compounds of phosphorus. Therefore, we are obliged to restrict ourselves to mentioning only a few more, that is, his work on dialkyl chlorophosphites (in collaboration with B. A. Arbuzov, and later with A. I. Razumov and V. S. Abramov), on phosphorous derivatives of pyrocatechin (with F. G. Valitova), on the determination of the dipolar moments of the organic compounds of phosphorus (dissertation of P. I. Rakov), on refractometry of organic compounds of phosphorus in connection with the atomic refraction of tri- and pentavalent phosphorus (with A. A. Ivanov), etc.

Work on the organic compounds of phosphorus, which was so splendidly begun by Arbuzov, in his early youth and successfully continued up to the present time, is undoubtedly among the most fundamental in this field and he may be considered as one of the founders of this branch. However, this is not the only reason why his work is of great importance to chemical science. It is also important due to the fact that with the aid of examples of the organic compounds of phosphorus he has thrown light on general problems of organic chemistry, such as the problem of tautomerism, homogenous catalysis of organic compounds, the obtaining of free radicals, etc.

His work, unrelated to the field of organic phosphorus compounds touches on various organic chemistry problems. We shall mention first the small cycle of experiments covering the interrelations of esters of sulfurous acid and alkyl sulfonic acids. He demonstrated that his method of regrouping can be applied also to some derivatives of sulfurous acid. Thus for example, the dimethyl ester of sulfurous acid is changed into the methyl ester of methyl sulfonic acid on heating with methyliodide:



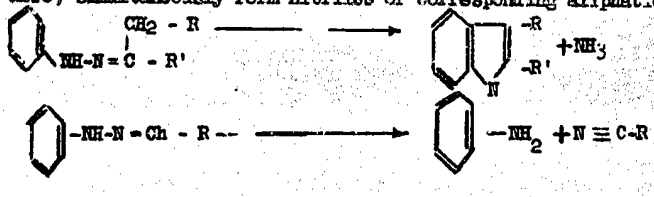
The same transformation takes place even at low temperatures, if the esters of sulfurous acid are subjected to saponification with a weak alkali solution in the presence of alkyl halides, but in this case the reaction is more complicated--through the intermediate stage of the sulfite of the alkali metal.

Further, it is necessary to mention Arbuzov's research work on reactions where the phenomena of catalysis plays an essential part. We have already mentioned that the part of catalysis in the transformation of organic combinations had repeatedly attracted his attention, and he was able to demonstrate conclusively the catalytic character of the regrouping of esters of phosphorous acid. He has also shown conclusively that the formation of ketone acetals, by Kleysen's method, with the aid of an orthoformic ester, takes place only in the presence of hydrogen ions of mineral acids and has a distinct catalytic character.

The reaction of acetal hydrolysis is of a similar nature, showing extreme sensitivity to the presence of mineral acids which in Arbuzov's opinion discloses a similarity to Kurtzius-Bredig's well-known reaction of the decomposition of ethyl diazoacetate. A detailed study of the hydrolysis of ketone acetals enabled Arbuzov to determine and compare two more of its peculiar features: irreversibility and a pronounced endothermic character. This necessitated careful thermochemical measurements, carried out by him with apparatus of his own design and, sometimes, manufacture. These measurements showed that the heat effect in the hydrolysis reaction of diethyl acetone acetal is 4.51 calories per gram-molecule.

We mention at this point that his interest in physicochemical research methods and his superior ability to make use of methods of exact physicochemical measurements have enabled Arbuzov to carry out a number of valuable experiments relating to other questions. Among them, we refer to his study of the reaction in the addition of bromine to ether, and his research work on the determination of specific volumes for liquid organic compounds at their boiling points.

Returning to Arbuzov's catalytic work, we also mention the reaction discovered by him in 1910, together with V. M. Tikhvinskiy, and elaborated in the course of subsequent research studies with other students, that is, the reaction of decomposition of aryl hydrazones of aldehydes and ketones in the presence of minute quantities of zinc chloride, cuprous chloride, and chlorides of certain other metals. Phenyl hydrazones of aldehydes and ketones form substituted indoles, and phenyl hydrazones of aldehydes with a sufficient molecular weight (C_4 or more) simultaneously form nitriles of corresponding aliphatic acids:



This fine reaction, in contrast to E. Fischer's well-known method for obtaining substituted indoles, also has a purely catalytic character and may be used as an excellent method for preparing certain indoles and nitriles.

In a group by itself is Arbuzov's work on the theory of tapping conifers and the discharge of soft resin from pines. In this work, which is extremely important from a practical standpoint, he has shown by means of very simple but absolutely reliable and convincing experiments that in the passages of resin in conifers there is a considerable pressure (2-3 atmospheres), which can be measured by a manometer. A procedure was worked out for the collection of resin from "wounded" pines into covered containers, which made it possible to more than double the amount of resin collected and also guaranteed its collection without loss of volatiles, the amount of the latter ranging from 35-36 percent in place of the 10-12 percent when collection was made by the regular method. Such an increase of profit in tree-tapping has helped to promote the growth of the tree-tapping industry in USSR, and has also made it possible to make a thorough study of the chemical composition of resin and turpentine extracted from the types of conifers found in our country. In this extensive work carried out by A. Ye. Arbuzov and his collaborators, one should mention particularly the experiments of B. A. Arbuzov, which threw new light on the composition of Russian turpentine.

Thus, in the chemistry of terpenes also, a division of organic chemistry which has received valuable contributions from the Kazan' school of chemists in the works of Flavitskiy and Vagner, Arbuzov has attained substantial results, going his own original way.

A review of his scientific activity would be incomplete if we did not mention his continuing and lively interest in the history of Russian chemistry, which he expressed in a series of outlines dedicated to the Kazan' school of chemists and its founders, Zinin and Butlerov, the great Russian scientists, the chemists Lomonosov and Mendeleyev, Lebedev and other outstanding representatives of Russian science. In all of his works on the history of chemistry, Arbuzov has noted the great influence exercised by Russian researchers on the development of world science, even though their work has not always received proper recognition.

In this connection, the most timely and significant outline is the one written by Arbuzov in 1945, regarding the influence of the work carried on by the Kazan' school of chemists on the development of the world chemical industry, from which it is clearly seen that the discoveries of the Kazan' chemists served as the foundation for such branches of chemical industry as the aniline dye industry, compounds of high-molecular weight, synthetic motor fuel, high-octane hydrocarbons, etc.

Such has been the many-sided scientific activity of A. Ye. Arbuzov abundant in accurate, logical, and convincing experiments and precise chemical thought. He is at the peak of his creative activity. Let us wish him many more years of work to the benefit of our country and science.

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